

A Review on the Application of Nucleation Theories in Thermoplastic Foams

M. Mokhtari Motameni Shirvan¹, M. H. N. Famili^{2*}, A. Golbang³

Polymer Engineering Group, Faculty of Chemical Engineering, Tarbiat Modares University, P.O Box: 14115-143, Tehran, Iran

¹mozaaffar.mokhtari@modares.ac.ir, ²nfamili@modares.ac.ir, ³a.golbang@modares.ac.ir

Abstract

The physical foaming agent is dissolved in the polymer at a pressure and temperature beyond its critical condition and the foam structure is formed by a sudden pressure drop or a temperature increase in the mixture in three steps; nucleation, growth and coalescence. In the nucleation step, due to a supersaturation, thermodynamic instability is formed in the mixture. This induces a tendency in the solvent molecules for a phase transition from a supersaturated state to a gas state in the direction of instability reduction. By overcoming the energy barrier, the free energy of the system is reduced and gas stable nucleuses are formed in the free volumes of the polymer chains. Growth and coalescence of the nucleuses take place with the diffusion of the gas molecules inside them. With increase in the nucleation efficiency, the growth and coalescence rate are reduced. Therefore, prediction of nucleation rate is an important factor for controlling the thermoplastic foam structures. Investigation of the nucleation step has been doable with the aid of nucleation theories. The classical nucleation theory is a prominent method for the investigation of nucleation phenomena in thermoplastic foams, but due to the existing of a divergence between its theoretical values with the experimental data, some modifications have been introduced into this theory. Other competing theories such as the Density Functional Theory and the Self Consistent Field Theory have also been developed. The main aim of this review paper is investigation of the existing theories and their modifications for thermoplastic foams.

Keywords

Thermoplastic Foam; Nucleation; Classical Nucleation Theory; Phase Transition

Introduction

Foams are materials in which gas cells are surrounded by a dense matrix. The first generation of thermodynamic foams had lower ductility and strength compared to pieces of solid polymers. This deficiency was resolved by reducing cell sizes in foam structures. In fact, cells with smaller dimensions in relation to a critical size can inhibit crack growth in the bulk. Thus, by developing such cells inside the material it is possible to reach pieces with decent mechanical properties and less material consumption [1, 2]. Based on this fact, investigation of the effective parameters for controlling cell size in thermoplastic foams has been carried out extensively and resulted in the production of microcellular foams. There has also been a considerable tendency for the development and production of nanocellular foams [2-18].

Both physical and chemical foaming agents can be used in the two common methods for the production of polymeric foams. When chemical foaming agents are incorporated, the foam's structure is usually formed in the polymer bulk due to a chemical reaction. In the first method such as polyuretan foams, Chemical foaming agents are the byproduct of the reaction between the polymer constituents in the form of gas which are trapped between the polymeric chains. In another method, such as aerogels and thermoset foams, the foam structure is formed by a chemical reaction resulting in a crosslinked three dimensional network [19-22]. On the other hand, when physical foaming agents are incorporated, it is dissolved in a polymer at a pressure and temperature beyond its critical condition and the foam structure is formed by a sudden pressure drop or a temperature increase in the mixture [23-25].

Physical foaming agents are used in continuous and batch processes in extruders and pressured vessels respectively, for the production of thermoplastic foams [2].

The foaming process is carried out during the following steps: nucleation, growth, coalescence and structure stabilization. After nucleation of gas molecules and development of stable nucleus, gas molecules diffuse inside the

nucleus and make them grow into cells. In case of a continuous growth, cells become connected and result in bigger cells [26, 27].

The main goal in this research is to review and discuss the current theories for the prediction of nucleation rate in thermoplastic foams produced by physical foaming agent by a sudden pressure drop.

The final foam structure is dependent on factors such as size, density, size distribution, dispersion and coalescence of cells. With increase in the efficiency of the nucleation stage, an additional number of molecules become involved in the nucleus production, thus on one hand there is less chance of cell growth and coalescence and on the other hand, there is an increase in cell density and a decrease in cell size. Therefore, this stage is a controlling factor in the foam structure. Study of the nucleation theories and recognitions of their strengths and weaknesses can significantly assist the control and prediction of the thermoplastic foams structure [28].

Mechanisms of nucleation phenomenon in thermoplastic foams are investigated using nucleation theories that are used to describe nucleation in first order phase transitions such as crystallization and boiling.

With the occurrence of super saturation and chemical potential difference in these processes, molecules are locally arranged beside one and other and fluctuations of energy and density are raised in the system. In case of exceeding the energy barrier, the free energy of the system is reduced and stable sites are formed in the first phase from the new phase which is followed by nucleation and phase transition. In thermodynamic science this phenomena is mainly modeled by classical and non classical methods. The aim of these theories is to investigate the effects of thermodynamically and kinematical variables and physical and chemical properties of constituents on the nucleation. The nucleation rate is predicted through the calculation of critical nucleation energy and the critical sizes of the newly formed regions in the new phase [29].

In the classical nucleation theory the new phase is assumed as a nucleus with a critical size which is separated distinctively from the former phase by a dividing surface.

In other words, the system is supposed to resemble an ideal model consisting of two homogeneous phases; old and new, and an imaginary dividing surface at the border between the phases. The thermodynamic properties of this system are a result of the thermodynamic properties of the two phases and the dividing surface. Additionally, the free energy of the system includes a volumetric part (two homogeneous phases) and a surface part (the dividing surface) [22, 23].

This theory consists of both homogeneous and heterogeneous nucleation. Homogeneous and heterogeneous nucleation occurs in the single phase primary mixture and in the presence of a second phase consisting of additive particles respectively. The second phase plays the role of the nucleation sites which cause a reduction in the nucleation energy and an enhancement in the nucleation rate [2, 29- 35].

The nucleation theory is applicable commonly for the calculation of nucleation rate in thermoplastic foams in the presence of a supercritical solvent. Although, the theoretical and experimental results do not show a proper consistency and in most cases only a correct pattern of changes may be predictable. Scientists have declared two main reasons for this inconsistency; error in the calculation of variables and simplifying assumptions for the establishment of the relations between variables. The variables include the interfacial tension between polymer and solvent, difference between the inside and outside pressure of the nucleolus. Other sources of error in this theory which should be taken into account are: absence of the effect of time, pressure drop rate and super saturation content. A lot of modifications have been suggested by various scientists to reduce the inconsistency. These attempts have been in a direction to care for the mentioned sources of errors which in some cases have resulted in superior outcomes [3, 36-41].

The presence of a number of small molecules in the nucleus and the assumption of an existing dividing surface on the border between the two phases raises uncertainty which cannot be resolved by this theory. To begin with, what exactly is a cluster? Are there any criteria physically for positioning the dividing surface? How can one determine the actual shape, structure and density of small clusters? How accurate is the use of specific surface energy as an independent factor from cluster size [29]?

Therefore in order to eradicate the mentioned misunderstandings in the field of thermodynamics, some

competitive theories with different approaches for the interpretation of first order phase transition have also been used from which we can point out to the density functional theory (DFT) and self consistent field theory (SCFT). The density functional theory is the basis of non classical methods for modeling of nucleation in the first order phase transition. In this theory, nucleation is considered as a local fluctuation of molecules' density. The free energy of the system is calculated on the basis of the fluctuations of density or weight fraction of the mixture components through the elimination of the dividing surface between the old and the new phases [38, 42-46]. It should be mentioned that this theory is used more often in the case of small molecules, but recently there have been some reports of its application in polymeric solutions for the calculation of mixture free energy and interfacial tension of solvent and polymer [45, 46].

In the SCFT theory, change in free energy is calculated versus the weight fraction of the mixture components and is used for the modeling of nucleation in polymeric foams. This theory is a mean field theory and is established for the study of non-uniform polymeric systems based on the equilibrium statistical mechanics in which there is no mention of time. In this theory, potential energy models such as Lenard-Jones (L-J) and mobility models such as Gaussian Chain model have been applied for the effects of molecular interaction between solvent and polymer and chain movements, respectively which will finally result in the derivation of free energy equation for a bubble in a compressible polymeric fluid versus the weight fraction. Due to the fact that these theories are based on molecular models, their findings have only been used for studying the effect of parameters, deeper understanding of nucleation and efficiency enhancement and thus are not comparable with experimental results [3, 47-53].

Nucleation in thermoplastic foams has also been studied from the perspective of phase separation kinetic in compressible polymeric solutions. Phase separation in polymeric solutions occurs with deviations of temperature, pressure and weight fraction of mixture components from the equilibrium state. The homogeneous mixture enters the unstable and metastable regions during phase separation and this phase separation takes place under nucleation, growth and spinodal decomposition mechanisms. This route depends on the amount and how of changes of temperature, pressure and weight fraction of mixture components. In a case where the system is pushed towards the totally unstable thermodynamic region the phase separation is the spinodal decomposition kind. If the system is pushed towards the metastable thermodynamic region which is between the binodal and spinodal lines, the phase separation mechanism is in the form of nucleation and growth. The spinodal decomposition results in the formation of a bi-continuous or a percolation microstructure. Meanwhile, the formation of separated regions in the matrix is due to the mechanisms of nucleation and growth [54-59].

Some models have been developed for further investigation of the behavior and kinetic of phase separation of compressible polymeric solutions. Regarding the interactions between gas and polymer molecules (e.g. formation of hydrogen bonds) in polymeric solutions, the mentioned models that include such effects is considered recently. The difficulties of the calculation of experimental parameters which are used in the models for the prediction of phase behavior of compressible polymeric solutions; application of models with less experimental parameters is more convenient [60-66].

There are also some reports on the use of light scattering and neutron scattering techniques for the study of the kinetics of phase separation in compressible polymeric solutions [67-69].

Due to the broadness of nucleation theories in the field of thermoplastic foams, the context of nucleation in thermoplastic foams from the point of view of phase separation kinetics in compressible polymeric solutions will not be reviewed. Thus, here an attempt has been made to initially study the nucleation phenomena and classical nucleation theory in thermodynamics and in the next step their applications, limitations and modifications for thermoplastic foams has been covered. Finally the density functional theory and Self Consistent Field Theory with their applications in polymeric solutions and thermoplastic foams have been reviewed briefly.

Nucleation in First Order Phase Transitions

Nucleation is the primary stage of first order phase transitions such as crystallization and boiling in which a substance can be transformed in to a stable state from a semistable. The transition from a metastable to an actual stable state occurs in the fluid to have a lower-energy state [22]. Generally, the thermodynamic driving force for the first order phase transition, chemical potential difference or supersaturation, is

$$\Delta\mu = (G_{\text{old}} - G_{\text{new}})/M = \mu_{\text{old}} - \mu_{\text{new}} \quad (1)$$

Supersaturation ($\Delta\mu$) is the gain in the free energy per molecule or (atom) in reference to the passage of the phase from the minimum with higher Gibbs free energy (G_{old}) to the minimum with lower Gibbs free energy (G_{new}). μ_{old} and μ_{new} are, the chemical potentials of the old and new phases at the cospending minima respectively [29,30].

For nucleation and phase transition of material in a specific period of time, a state of supersaturation as well as an energy level higher than the energy barrier is required [29].

As an example, the transition of the Van der Waals (VDW) fluid with below equation of state from liquid phase (old phase) to gas phase (new phase) for better understanding of first order phase transition is expressed.

$$(P + M^2 a' / V^2)(V - Mb') = MkT \quad (2)$$

Where P and V are fluid pressure and volume, respectively, M is the number of molecules (or atoms) in this volume, T is the absolute temperature, K is the Boltzman constant, and a' and b' are material constants accounting, respectively, for the molecular interactions and molecular volume. These two constants can be written in terms of the critical pressure P_{cr} volume V_{cr} and temperature T_{cr} of the VDW fluid using the following relations:

$$P_{\text{cr}} = a' / 27b'^2 \quad V_{\text{cr}} = 3Mb' \quad T_{\text{cr}} = 8a' / 27kb' \quad (3)$$

The VDW fluid equation of state and free Gibbs energy can be expressed by equations 4 and 5, respectively, using the appropriate relations for reduced pressure $P' = P/P_{\text{cr}}$, volume $V' = V/V_{\text{cr}}$ and temperature $T' = T/T_{\text{cr}}$.

$$(P' + 3/V'^2)(3V' - 1) = 8T' \quad (4)$$

$$G(V', T') = G_{\text{ref}}(T') + MkT_{\text{cr}}[3V'T'/8 - 9/8V' - T'\ln(3V' - 1)] \quad (5)$$

Nucleation in phase transition from a liquid state to a gas state in constant temperature with volume changes has been investigated using the phase diagram of the VDW fluid and changes in energy shown in figures 1 and 2.

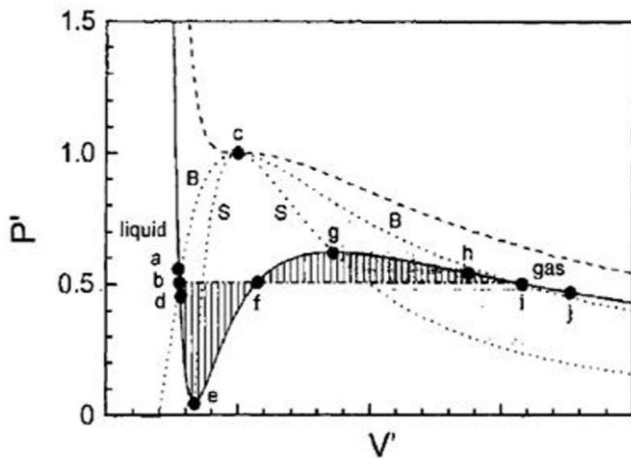


FIG 1. DEPENDENCE OF REDUCED PRESSURE OF VDW FLUID ON REDUCED VOLUME [29]

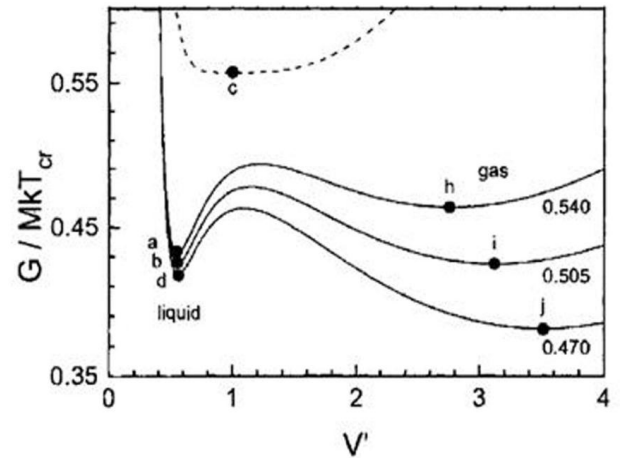


FIG 2. DEPENDENCE OF GIBBS FREE ENERGY OF VDW FLUID ON REDUCED VOLUME [29]

In case the initial material phase is in the state of liquid, with a certain temperature and pressure and a volume equivalent to point a in figure 1, its volume has to increase to point h in order to undergo a phase transition to the gas phase in the same temperature and pressure. The most probable phase transition route is through a uniform change in material density and an increase in its volume. According to figure 2, the free energy increase initially, reaches a maximum and reduces in the route with an increased volume. So the free energy difference of points a and maxima is the energy barrier of uniformly changing density route. Considering the amount of required energy for exceeding the energy barrier of the mentioned route, it is understood that phase transition is thermodynamically unfavorable [29, 30].

Another conceivable phase transition path with much less energy consumption in comparison to the first path is known as the non-uniform change of the density of the old phase into the density of new one through local changes and fluctuation of density in a contracted spatial region by a small number of molecules.

If M and n^* are, respectively, the number of total molecules and the number of molecules in the spatial region of locally changed density, the energy barrier for the phase transition corresponding to the nonuniformly changing density ($n^* \Delta\mu$) is much less than the energy barrier for the path corresponding to uniformly changing density ($M\Delta\mu$) and thus the possibility of first order phase transitions to occur by local density fluctuations is generally greater than by uniform change of the density of the old phase.

Many observations such as rains, snowfalls and experimental investigations suggest that the path followed in reality by a first-order phase transition is in fact the appearance of nanoscale formations with density close to that of the new phase which are randomly formed in the old phase and the termination of phase transition by the overgrowth of the new phase to larger sizes. So, what is meant by nucleation is actually the process of random generation of those nanoscopically small formations of the new phase which are capable of irreversible overgrowth to macroscopic sizes.

As stated previously, mechanisms of nucleation phenomena in thermoplastic foams have been studied from a view point of first order phase transition of solvent molecules (gas) from a supersaturated state to a gas state in a polymeric matrix. The existing theories have been used effectively in this field. In continue, first the classical nucleation theory and then its application in thermoplastic foams will be looked.

Classical Nucleation Theory (CNT)

In the Classical nucleation theory, nucleation presumably occurs in the new phase in the form of nucleus with a critical size and it is separated from the old phase by a dividing surface and thus the molecules of the old and new phases are separated.

In other words, after a phase transition the system is supposed to be made up of two uniform and distinguishable old and new phases and a dividing surface as demonstrated in the model in figure 3.

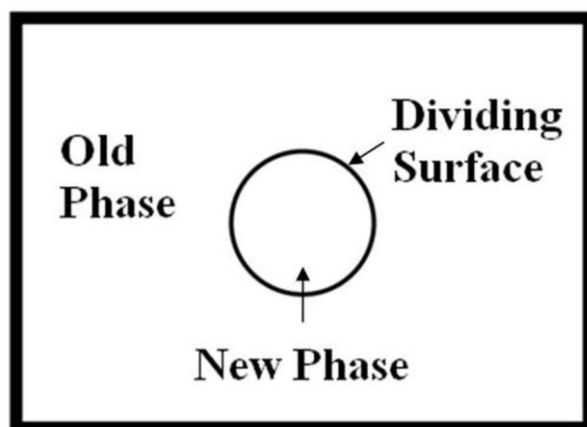


FIG 3. SCHEMATIC VIEW OF OLD AND NEW PHASES AND DIVIDING SURFACE

In this theory, two types of homogeneous and heterogeneous nucleation exist which are distinguishable. Homogeneous nucleation takes place in the initial single phase mixture and heterogeneous nucleation also occurs in the presence of a second phase such as additives. The second phase plays the role of nucleation sites and reduces the nucleation energy while increasing the rate of nucleation [30].

In this theory, the mechanism of changes in the system free energy due to the formation of a nucleus from the new phase in the old phase is investigated in equilibrium thermodynamics. Based on this theory, in the case of a uniform liquid serving as the initial phase, due to phase transition it will be transformed into a nucleus with a distinct boundary in the gas phase which is surrounded by the initial liquid phase.

In general, the total energy of a homogeneous part of the system is a sum of the energies of the surface (no volume $V = 0$), and bulk (no surface area $A = 0$) contributions.

$$U = T_0 S - PV + \sigma A + \sum \mu_i N_i \quad (6)$$

Which U , T_0 , P , S , V , A , σ , μ_i , N_i are internal energy, temperature, pressure, entropy, volume, surface area,

interfacial tension, chemical potential and the number of molecules of system components respectively.

So the initial energy of the homogeneous liquid is

$$U_0 = T_0 S_0 - P_0 V_0 + \sum \mu_{i,l}^0 N_{i,l}^0 \quad (7)$$

Which $U_0, T_0, P_0, V_0, \mu_{i,l}, N_{i,l}$ are the thermodynamic characteristics of homogenous liquid phase.

The final energy in the system consisting of the vapor cluster surrounded by liquid is

$$U = T_0 S - P_g V_g - P_L V_L + \sigma A + \sum \mu_{i,g} N_{i,g} + \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,s} N_{i,s} \quad (8)$$

Which $P_g, V_g, \mu_{i,g}, N_{i,g}, \sigma$ are pressure, volume, chemical potential, number of molecules of cluster and interfacial tension between liquid phase and cluster. V_L, P_L are volume and pressure of liquid phase and $\mu_{i,s}, N_{i,s}$ are chemical potential and number of molecules of surface respectively.

When a droplet is formed in a vapour, three choices exist for the free energy which depends on the conditions of the real nucleation process (in nature or laboratory) or the hypothetical mind experiment. In turn, the suitable free energy is related to the quantities which are held constant when the droplet forms.

If the pressure of the liquid is constant $P_l = P_0$ and the total molecular numbers are unchanged $N_{i,tot} = N_{i,l} + N_{i,g} + N_{i,s} = N_{i,l}^0$ then the Gibbs free energies in the initial and final states are

$$G_0 = U_0 - T_0 S_0 + P_0 V_0 = \sum \mu_{i,l}^0 N_{i,l}^0 \quad (9)$$

$$G = U_0 - T_0 S + P_0 V_{tot} = U - T_0 S + P_0 (V_g + V_L) = (P_0 - P_g) V_g + \sigma A + \sum \mu_{i,g} N_{i,g} + \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,s} N_{i,s} \quad (10)$$

The Gibbs free energy change in the droplet formation for equilibrium thermodynamic is

$$\Delta G = (P_0 - P_g) V_g + \sigma A + \sum \mu_{i,g} N_{i,g} + \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,s} N_{i,s} - \sum \mu_{i,l}^0 N_{i,l}^0 \quad (11)$$

Regarding the difficulty of measuring the thermodynamic properties of surface and nucleus, a few assumptions are set to ease the calculation of nucleation free energy and to estimate the free energy based on the available thermodynamical properties which will be reviewed in the following section.

By assuming that the composition of the liquid phase is constant, which according to the Maxwell equation and state of constant pressure denotes the constancy of chemical potential $\mu_{i,l} = \mu_{i,l}^0$ and knowing that the total molecular numbers are unchanged, we reach:

$$\Delta G = (P_0 - P_g) V_g + \sigma A + \sum (\mu_{i,g} - \mu_{i,l}^0) N_{i,g} + \sum (\mu_{i,s} - \mu_{i,l}^0) N_{i,s} \quad (12)$$

When the liquid volume is large and the cluster is small, its formation does not significantly change the state of the liquid. In this case, equilibrium can be accomplished by setting the derivatives of ΔG to zero. The equilibrium is reached by maintaining the pressure p_o and chemical potential $\mu_{i,l}^0$ at constant levels and considering the deviations in accordance to:

1. V , keeping $N_{i,g}$ and $N_{i,s}$ constant.
2. $N_{i,g}$, keeping $N_{j,g}, j \neq i$ and $N_{i,s} \forall i$ constant.
3. $N_{i,s}$, keeping $N_{j,s}, j \neq i$ and $N_{i,g} \forall i$ constant.

and setting these derivatives equal to zero.

$$P_g^* - P_0 = \left(dA/dV_g \right) \sigma^* = \left(\frac{2\sigma^*}{r^*} \right) \quad (13)$$

$$\mu_{i,l}^* = \mu_{i,s}^* = \mu_{i,g}^* \quad (14)$$

Equilibrium is denoted by (*).

By replacing equations 13 and 14 into equation 12, the change in free energy due to the formation of a nucleus from the gas phase in the initial liquid phase at equilibrium is achieved. If the nucleus is assumed to be spherical then we have:

$$\Delta G^* = (P_0 - P_g^*)V_g^* + \sigma^* A^* = -\frac{2\sigma^*}{r^*}V_g^* + \sigma^* A^* = -\frac{2\sigma^*}{r^*}\frac{4}{3}\pi r^{*3} + 4\pi r^{*2}\sigma^* = \frac{4}{3}\pi\sigma^* r^{*2} \quad (15)$$

If, the homogeneous relations of equilibrium radius and equilibrium free energy are [29,30]:

$$r^* = \frac{2\sigma^*}{\Delta P^*} \quad (16)$$

$$\Delta G^* = \frac{16\pi\sigma^{*3}}{\Delta P^{*2}} \quad (17)$$

Classical Nucleation Theory in Thermoplastic Foams

As stated previously, in the case of thermoplastic foams, the physical foaming agent (usually a gas) is dissolved in polymer at a pressure and temperature higher than the critical condition. Foam is developed through a pressure drop of the solution. Incorporation of the classical nucleation theory for the prediction of the nucleation rate in microcellular foams was initially carried out by Martini, Youn and Colton in MIT University in the 80s and since then it has been used continuously in the field of thermoplastic foams [2, 3, 26, 27, 70].

(1) Homogenous Nucleation

In order to apply this theory for thermoplastic foams, after a pressure drop the resultant mixture is assumed to consist of solvent molecules in gas state surrounded by a polymeric layer as the old phase. A Change in free energy of the equilibrium state for the formation of spherical gas nucleus in polymer is expressed by equations 18 and 19 which is similar to relation 14.

$$\Delta G = -V \Delta P + A\sigma \quad (18)$$

$$\Delta G = \frac{4}{3}\pi r^3 \Delta P + 4\pi r^2 \sigma \quad (19)$$

ΔP is the difference in pressure between inside and outside of a cluster. This term can usually be replaced by pressure difference between saturation and atmospheric pressure in very fast depressurization. r is the cluster radius and γ is the microscopic interfacial tension of polymer and gas cluster which for a flat surface is usually assumed to be equal to the macroscopic interfacial tension between polymer and gas solvent.

Changes of droplet formation free energy with cluster radius is demonstrated in figure 4. It is realized that the interfacial term increases with r^2 and the potential difference decreases with r^3 , thus, the creation of small bubbles lead to a free energy increase to the extent where the radius of the bubble nucleated is larger than a critical size relative to a maximum free energy. The critical size of cluster and maximum free energy are represented by critical radius and critical nucleation energy respectively [1].

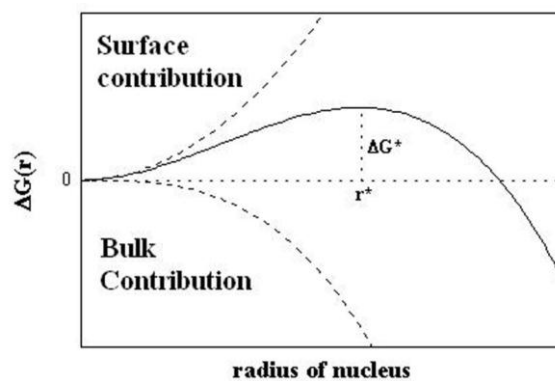


FIG 4. CHANGES OF NUCLEUS FORMATION FREE ENERGY WITH ITS RADIUS

Critical radius and energy in equilibrium state are expressed with equations 15 and 16 which are equivalent to the extremum point of equation 18.

Homogeneous nucleation rate on the basis of Boltzmann relation is expressed

$$J = f_0 C_0 \exp(-\Delta G_{hom}^*/KT) \quad (20)$$

Which f_0 and c_0 are frequency factor as a probability of gas molecules interaction to nucleuses and solvent

concentration respectively [2, 26, 27, 70]. In nucleation literature, nucleus formation kinetic is investigated on the basis of probability of attachment and detachment of molecules to nucleuses as an effect of interaction [30].

(2) Heterogeneous Nucleation

Addition of a second insoluble phase (solid particles) to the solution leads to a heterogeneous nucleation. The interfacial tension is reduced and the nucleus develops in the interface with the addition of the second phase known as the nucleation agent or nucleation site. As illustrated in figure 5, the nucleus set a wetting angle θ with the surface of particle. The relation for stress equilibrium is presented as:

$$\gamma_{ls} = \gamma_{gs} + \cos \theta \gamma_{gl} \quad (21)$$

$\gamma_{ls}, \gamma_{gs}, \gamma_{gl}$ are interfacial tension of solid-liquid, gas-solid and gas-liquid phases. Additive particles, solvent and polymer are formed solid, gas and liquid phases respectively.

From relation 21

$$\cos \theta = (\gamma_{ls} - \gamma_{gs}) / \gamma_{gl} \quad (22)$$

Heterogeneous critical nucleation energy in equilibrium state is

$$\Delta G_{het}^* = -V\Delta\mu + A_{gl}\gamma_{gl} + A_{gl}\gamma_{gs} - A_{ls}\gamma_{ls} \quad (23)$$

$$\Delta G_{het}^* = \Delta G_{hom}^* S(\theta) \quad (24)$$

$$S(\theta) = \left(\frac{1}{4}\right) (2 + \cos \theta)(1 - \cos \theta)^2 \quad (25)$$

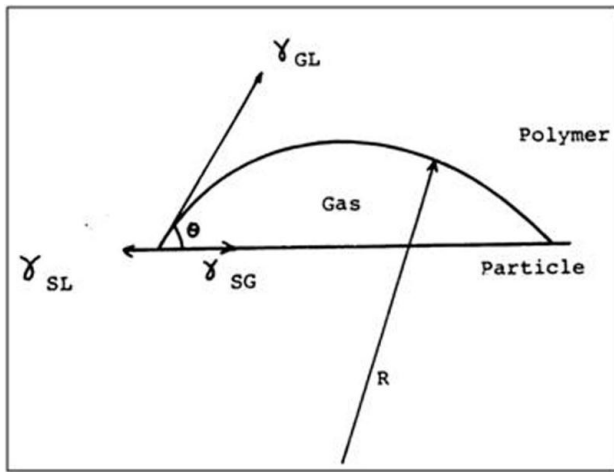


FIG 5. INTERFACIAL TENSIONS OF HETEROGENOUS NUCLEATION

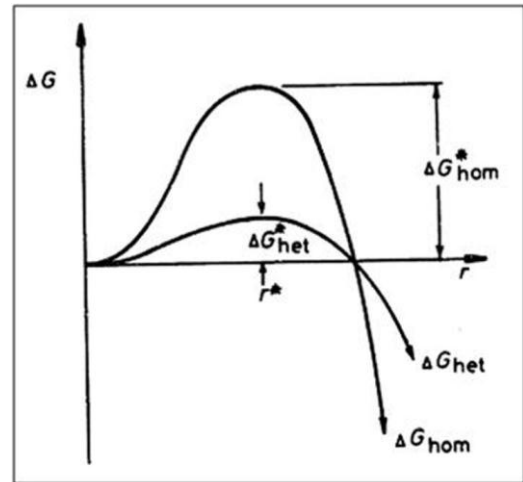


FIG 6. CRITICAL HOMOGENUES AND HETEROGENOUS NUCLEATION ENERGIES

Because $S(\theta)$ is always smaller than one, according of equation 24, heterogeneous critical nucleation is smaller than homogeneous state and its nucleation rate is increased. Heterogeneous nucleation rate is

$$J_{het} = f_1 C_1 \exp\left(-\Delta G_{het}^* / KT\right) \quad (26)$$

Which f_1 and c_1 are frequency factor and solvent concentration respectively [2,70 -87].

Weaknesses of the Classical Nucleation Theory

Application of the classical nucleation theory for the assessment of thermoplastic foams nucleation rate in the presence of a supercritical solvent in the batch process is common. Nevertheless, the theoretical results do not have appropriate consistency with the experimental results and in many cases this theory is only able to give a decent prediction about the trends of changes. The reasons behind this inconsistency will be discussed in this section [3-9, 26-29,38-41, 50].

As explained in section 2-1, the relations applied for the calculation of nucleation rate is based on equilibrium thermodynamic of the system, however, nucleation in fact is a nonequilibrium and irreversible process and its path is very effective and determining in the final efficiency. Due to the complications of performing the nonequilibrium thermodynamic method, scores number of studies has been conducted in this field so far mainly in relation to small molecules [88].

Scientists identify other factors for this inconsistency which originate from the assumptions for simplification of the relations of classical nucleation theory. As states in former sections, the assumptions are as follows:

1. The thermodynamic properties of nucleus in nanoscale are equivalent to thermodynamic properties of the bulk in macroscopic scale (equation 13).
2. The interfacial tension difference of nucleus in a nanoscale with a curved surface is equivalent to the macroscopic interfacial tension difference between two bulks with a smooth surface which is also known as the capillary effect.
3. With assuming an instantaneous pressure drop, the pressure difference between the inside and outside of the nucleus is considered to be equivalent to the pressure difference between the initial and the end of the process [3, 38, 53, 89-97].

The effect of the stated assumptions is even more apparent with decrease in cell size which extends the inconsistency between the theoretical and experimental results [3, 38]. Ignoring the factors related to pressure drop rate or time, supersaturation level and the presence of polymeric chains in these relations results in the prevalence of errors in calculations [40,55,87]. With regard to the mentioned statements, some scientists have made some modifications on this theory which will be pointed out in the upcoming section.

Modifications for the Classical Nucleation Theory

The source on inconsistency between the experimental and the theoretical results is recognized as the incorrect calculation of energy and the nucleation rate for the modeling of nucleation phenomenon with the use of nucleation energy relation (equation 17). The incorrect calculation of nucleation energy can be due to two reasons; low precision in the models and experiments for the calculation of the nucleation energy experimental parameters and not including all the effective factors in it. Thus, the modifications performed on this theory for the thermoplastic foams are also categorized into two methods; the exact calculation of variables and inclusion of other variables affecting the amount of nucleation energy to the mentioned relation. The modifications on this theory are developed extensively in small molecules and there has been an attempt to eliminate the simplifying assumptions for the derivation of nucleation energy relation [90-97].

For the exact calculation of CNT variables, some equation states such as Non Random Hydrogen Bonding (NRHB) and Sanchez-Lacombe (SL) are used for calculation of the nucleation energy experimental parameters[98-99].

A tremendous amount of work has been carried out by Colton and Suh, Han and Han, and Goel and Beckman. Shafi and Flumerfelt, Ohshima and his co-workers, and Sirupurapu et al work on predicting bubble nucleation in thermoplastic polymers using classical nucleation theory [87].

Colton and Suh applied the classical nucleation theory to assess the rate of nucleation in microcellular polystyrene foams, carbon dioxide gas and zinc stearate particles and became aware of the inconsistency between the theoretical and experimental results due to error in the evaluation of interfacial tension. Then, they introduced the effects of polymeric chains in the nucleation energy through specific assumptions.

Colton and Suh also investigated the effect of the presence of soluble and insoluble additives in a solution on the nucleation energy. They assumed that, a dissolved additive increases the free volume and distance between polymer chains. If the solubility limit of the additive is exceeded, the additive will precipitate and form particles as a second phase and nucleation will be heterogeneous. The ability of the particles to act as nucleation sites can be calculated by determining the degree of bonding between the particles and the polymer. If there is a high degree of bonding, a large amount of energy will be required to force the interface apart. If this energy is high enough, nucleation may be precluded. If a poor bond exists, the interface will have a large amount of energy associated with it and will enhance nucleation [27,70]. However, they did not take into account the effects of interaction

between particles and polymer on the distribution and dispersion quality of particles and its effect on the final foam structure.

Nucleation is affected from local change of free volume with pressure and additive particles in their model. The Lennard-Jones model which approximates the potential energy of two non-interacting molecule for modeling of interaction energies has been used. The interaction between the electric fields of the negative electrons and the positive nuclei give rise to forces of interaction between any pair of molecules, which depend on the nature of the molecules and the distance separating them [2,27,70].

In the Lennard-Jones model the sum of the attractive (London or dispersion forces) and repulsive forces and potential energy function for spherical molecules is given by

$$F = K_R r^{-13} + K_L r^{-7} \quad (27)$$

$$U(r) = \left[\frac{-K_R}{12} \right] r^{-12} - \left[\frac{-K_L}{6} \right] r^{-6} \quad (28)$$

In which r is the molecular distance. The Lenard-Jones potential function is commonly written in the form of

$$U(r) = 4\varepsilon \left\{ \left[\frac{-\delta}{r} \right]^{12} - \left[\frac{-\delta}{r} \right]^6 \right\} \quad (29)$$

ε is the maximum energy of attraction is one value of r for $u(r) = 0$.

In their assumptions, the polymer molecules are as the gas molecules in the L-J model with a potential energy that varies with the distance between them. Solvent and particles also increases the intermolecular separation by occupying the interstitial space between the molecules. The effect on the free volume would be proportional to the solubility. Both of these effects act to increase the potential energy of the system. These effects has quantified into a coherent expression [2,27,70].

The molar volume of a polymer consists of four terms: a reference volume at a reference temperature and pressure, volume changes due to temperatures difference from the reference, any internal gas pressure and any additives in solution.

$$V(T, P, C) = [V_0 + \alpha(T - T_0)] + \left(1 + \frac{P_{sat}}{3B(T)}\right) + (Volume\ of\ additive) \quad (30)$$

Where V_0 is the molar volume of the polymer repeat unit at a reference temperature, α is the coefficient of thermal expansion of the polymer, T_0 is the reference temperature, T is the temperature, P_{sat} is the saturation pressure of the gas in the polymer, $B(T)$ is the bulk modulus of the polymer at temperature T .

Polymer molecules can be modeled as points with spherically symmetric potential fields.

The volumetric molar mass is related to the distance between polymer molecules:

$$a = 2 \left(\frac{3}{4\pi N} V_w \right)^{1/3} \quad (31)$$

$$R(T, P, C) = 2 \left(\frac{3}{4\pi N} V(P, T, C) \right)^{1/3} \quad (32)$$

By replacing R in the potential energy relation we come to:

$$U(R) = U_0 \left[\left(\frac{-R_0}{R} \right)^{12} - 2 \left(\frac{-R_0}{R} \right)^6 \right] \quad (33)$$

Where U_0 is the equilibrium potential energy. Thus, changes in the potential energy of the polymeric molecules originating from the presence of gas and additives can be calculated. Potential energy relative to changes in pressure and concentration of additives show a stronger and weaker dependency respectively and increase in the distance between polymer chains enhances the variations in the potential energy [26,48].

Colton and Suh included the potential energy in their calculations of nucleation energy but did not reach acceptable results which they assumed to originate from the incorporation of J-L potential energy model. The free volume model was proposed as the first methods for the modification of the thermoplastic foam version of the classical nucleation theory for resolving the mentioned inconsistency, although there have been criticizes on the

model and its assumptions [2, 27,70].

In another investigation, an attempt was made to reduce the errors of the classical nucleation theory for the prediction of energy and rate of nucleation in polymeric foams by Han and Han [40].

Which the effect of polymer chain and super saturation on nucleation energy can be expressed by the following relation:

$$\Delta G_t = K_B T [Ln\varphi_1 + \varphi_2 + \chi\varphi_2^2] \quad (34)$$

$$\Delta G_s = nK_B T Ln\left(\frac{P_G}{P_V}\right) \quad (35)$$

Where φ_1 and φ_2 are the volume fractions of solvent and solute, respectively, χ the interaction parameter, n is the number of solvent molecules in a critical bubble, P_G is and pressure of the gas inside the nucluous, P_V is the equilibrium vapour pressure and $\left(\frac{P_G}{P_V}\right)$ is the super saturation level.

Thus,

$$\Delta G_p^* = \Delta G^* - \Delta G_t - \Delta G_s \quad (36)$$

Where, ΔG^* is the critical energy of the classical nucleation theory.

Finally they have calculated the density of cells theoretically and evaluate their consistency with experimental results. The theoretical results have higher values in comparance to experimental results. The reason for this inconsistency is recognized as the coalescence of nucleuses. Despite the unpleasantness of this outcome, usually the results gained from the classical nucleation theory exhibit smaller values of cell density and nucleation rate compared to the experimental results which stands as a proof for the effectiveness of the performed modifications [40,55].

Some of the studies for the evaluation of the parameters of the classical nucleation energy relation with more precise methods will be reviewed in this section.

The variants of the nucleation energy relation are the difference between the interfacial tension of the polymer and the solvent nucleus and also the difference between the inside and outside pressure of a nucleus which are respectively equivalent to the difference between the macroscopic interfacial tension of a smooth surface between solvent and polymer and also the pressure difference of the saturation stage and atmosphere in foaming process. The macroscopic interfacial tension is strongly dependent on factors such as temperature, pressure and weight fraction of solvent in polymer. In order to estimate the solvent weight fraction (usually a gas), one has to calculate its density at a specific thermodynamic condition with the use of an appropriate equation of state [39,98-100].

Satish and his coworkers have developed polymethylmethacrylate foams in a batch process with the incorporation of carbon dioxide. They traced the effects of pressure and temperature changes in the ranges of 0 to 35 MPa and 40 to 80 °C on the amount of gas absorption, interfacial tension between gas and polymer, nucleation energy and critical radius, theoretically using the modified mean field lattice- gas theory (MFLG). They also managed to calculate the nucleation rate experimentally and theoretically through the use of homogeneous classical nucleation theory. A summary of their results will be reviewed presently [39,101].

The following relation can be used for the calculation of the Interfacial tension between the polymer and gas phase.

$$\gamma_{mix}^{1/4} = \bar{Q}_{mix} \sum_{i=1}^2 \frac{x_i \gamma_i^{1/4}}{Q_i} \quad (37)$$

Where, x_i , Q_i and γ_i are respectively the molar fraction, molar density and interfacial tension between the components of a mixture. Knowing that the interfacial tension of a supercritical fluid is zero, by replacing molar density with mass density (g/cm³) we have:

$$\gamma_{mix} = \gamma_{polymer} \left(\frac{\rho_{mix}}{\rho_{polymer}} \right)^4 (1 - w_{gas})^4 \quad (38)$$

Where w_{gas} is the weight fraction of the absorbed gas in polymer at saturation. With the calculation of weight fraction of the absorbed gas and mass density of the mixture using the MFLG model or any other suitable equation of state for the polymer-solvent solution at high pressure, the mixture interfacial tension will be reached and the values of critical radius, critical energy and nucleation rate at various temperature and pressure condition will be found. The number of nuclei can be estimated using the relation below:

$$N_{\text{total}} = \int_0^t J dt = \int_{p_{\text{sat}}}^{p_0} J \frac{dp}{dp/dt} \quad (39)$$

Where P_{sat} and P_0 are the saturation and atmospheric pressure respectively.

In addition, the number of cells can be assessed experimentally using the SEM results with the relation below:

$$N_{\text{f}} = \left(\frac{nM^2}{A} \right)^{3/2} \quad (40)$$

Where n , M and A are the number of cells in the SEM image of the foam, magnification and the image area.

According to the experimental results, pressure increase and pressure drop rate and also temperature reduction result in an improved nucleation. Changes in carbon dioxide absorption in polymer with pressure and temperature, changes in interfacial tension of polymethylmethacrylate with temperature variations of its glass temperature with pressure were discussed and the results have a decent consistency with the experimental data. Comparison between the number of nucleus from relations 50 and 51 indicate an acceptable consistency between the theoretical and experimental results especially at pressures above 20 MPa [39].

Thus, the results gained from this study confirm the possible reduction of the existing errors between the experimental and theoretical results in some experimental conditions with the precise calculation of the experimental parameters of the classical nucleation theory with a suitable equation of state.

In a study on foaming of polystyrene and polylactide with carbon dioxide at various temperatures and pressures, the classical nucleation theory and the Non-Random Hydrogen-Bonding (NRHB) were used for the prediction of results [87].

The NRHB state equation is frequently used to investigate the thermodynamic behavior of gas and liquid phases, supersaturation state, polymeric solutions and also for the evaluation of gas absorption or supersaturated fluids in polymers and its effect on plasticization [98, 99].

Based on the experimental data, increase in pressure and pressure drop rate and decrease in temperature results in an improved nucleation. In addition, with the used of the NRHB model it has become possible to assess and monitor the changes in carbon dioxide absorption in polymers, variations of interfacial tension of polystyrene, changes in its glass transition temperature with pressure and temperature and the final results have demonstrated a decent consistency with the experimental data.

The changes in nucleation energy, cell density and critical nucleus size with pressure and temperature and have also been studied using the values obtained from the thermodynamic model and the classical nucleation theory. Qualitative analysis of changes in nucleation energy in regard to the size of critical nucleus and a quantitative analysis of cell density in relation to experimental data approves the capability of the classical nucleation theory for accurate prediction of results both quantitatively and qualitatively in case of using correct values of data [98].

Thus, in some cases the experimental data for microcellular foams have good consistency with the classical nucleation theory and its modifications, although the inconsistency increases with the reduction of cell size [50].

Density Functional Theory

In the unstable region of the phase transition diagrams, fluctuations of temperature, density or pressure are in a limit where the energy barrier is conquered and phase transition occurs, while the classical nucleation theory does not predict a reduction of the energy barrier around or inside the unstable region. In the classical nucleation theory the thermodynamic properties of nucleus are calculated based on the thermodynamic properties of the bulk and a distinctive boundary is presumed between the nucleus and the bulk, while no exact boundary can be predicted physically. In this theory the interfacial tension is considered between the bulk and the macroscopic nucleus and is

calculated by assuming a smooth and curveless boundary which is the source of error. Therefore, in order to overcome such a conspiracy, the density functional theory can be incorporated for the modeling of nucleation [42-49, 102-103].

In statistical mechanics, the macroscopic thermodynamic methods and methods based on microscopic simulation, the density functional theory is a new method for the study of substances. In this technique the molecular details of substances are used for the development of a rational calculation time and an acceptable physical sense [102-103].

In this theory, nucleation is considered as a local density fluctuating of molecules and with the elimination of the dividing surface between the new and old phases; the free energy of the system is calculated based on the fluctuations of density or component compositions.

If $\rho(r)$ is regarded as the density of molecules at point (x,y,z) with a position vector of $r(x,y,z)$, then space inhomogeneity or fluctuations of the molecular density of the system is expected which results in the fluctuations of quantitative properties. The free local Helmholtz energy per molecule f is a function of r , density and its derivations and the free energy of system in the two phase condition is expressed as:

$$f_2(Q) = \int_V f(r)q(r)dr \quad (41)$$

Which $q(r)dr$ is the number of molecules in an infinitesimal differential volume of $dr = dx dy dz$ around point r .

For the free Gibbs energy we have:

$$G_2 = F_2 + PV \quad (42)$$

Equation (52) is a function of density function. When a function is dependent on another function, it is known as a functional.

In the density functional theories, the work of nucleation w is a function of density function.

$$G_2\{Q\} = \int_V [f(r) q(r) + Q]dr \quad (43)$$

For the work of nucleation we have:

$$w\{Q\} = \int_V \{ [f(r) - \mu_{old}] q(r) + Q \} dr \quad (44)$$

Relation (55) is the work of formation of density fluctuation with a profile $q(r)$ in a single component system which there is no difference between the new phase and the bulk [29, 30].

The critical work of nucleation w^* , is a special form of work for the formation of density fluctuation:

$$w^* = w\{Q^*\} \quad (45)$$

Where,

$$(\partial w \{Q\})_{Q=Q^*} = 0 \quad (46)$$

$\rho^*(r)$ is obtained from solving equation (57).

The free energy function $f(r)$ has to be known for solving equations (57) and (56). The most common way to define this function is through the potential molecular functions.

Cahn and Hilliard used the density functional theory for the investigation of nucleation in a two component fluid for the first time in which the free energy is calculated based on the regular solution. Their results for critical nucleus were in contrast with the results obtained from the classical nucleation theory which by approaching the unstable region, nucleus size is increased while nucleation energy is reduced.

This theory has been used in many cases for the evaluation of nucleation. In some studies, the effects of size and surface curvature of nucleus on interfacial tension has been calculated using this theory and the achieved results have been used in the classical nucleation theory. Additionally, the value of the nucleation energy calculated from this equation is found to be less than that of the classical nucleation theory. The theories based on this standpoint have also been used to assess the nucleation energy in polymeric foams. Since these theories are based on

molecular models, thus their results are only sufficient for investigating the effects of various parameters and insight into nucleation process and methods of promoting its efficiency. However, these results are not comparable to the experimental results. Because, first, the materials studied experimentally are relatively complex and may not be describable by simple spherical potentials. Second, nucleation rates are exponentially sensitive to almost everything in the calculation; a small error in calculating the surface tension from first principles could translate into a huge error in the predicted nucleation rate [3, 42-49, 104-105].

Self Consistent Field Theory (SCFT)

The similar sizes of polymer chains with high molecular weight has manifested the role of global polymer behavior over the effect of atomic details for characterization and development of common theories for modeling of polymeric systems. Another feature of polymeric systems is the many number of configurations which results in contact between a polymer molecule and many other molecules and reduce the effect of intermolecular forces. These characteristics have made the incorporation of mean field theories possible for modeling and description of polymeric systems [103,106].

Self consistent field theory, the most applicable mean field theory with fundamental and reliable assumptions commonly is used for the study of polymeric blends, polymer absorption at surfaces, microphase separation in block copolymers and phase separation in blends and polymeric solutions. This theory is an expression of the changes in free energy of polymeric solutions with variations of composition which is regarded to be in competence with the density functional theory for the calculation of nucleation energy in polymeric foams [103,106-110].

The free energies of a fluid bubble in a polymeric solution and single phase polymeric solution can be calculated using the SCFT with the following relations:

$$\mathcal{F} \equiv \frac{NF}{\rho_0 k_B T V} = -(1 - \phi_s) \ln \left[\frac{Q_p}{V(1 - \phi_s)} \right] - \frac{Q_s}{\alpha} \ln \left(\frac{Q_s \alpha}{V \phi_s} \right) + \frac{1}{V} \int dr \left[\chi N \phi_p(r) \phi_s(r) - w_s(r) \phi_s(r) - w_p(r) \phi_p(r) \right] \quad (47)$$

$$\mathcal{F} \equiv \frac{NF}{\rho_0 k_B T V} = (1 - \phi_s) \ln(1 - \phi_s) + \frac{\phi_s}{\alpha} \ln \left(\frac{\phi_s}{\alpha} \right) + \chi N (1 - \phi_s) \phi_s \quad (48)$$

Where the $\phi_p(r)$ and $\phi_s(r)$ are the local volume fractions of polymer and solvent respectively, $(1 - \phi_s)$ and ϕ_s are the global volume fraction of polymer and solvent respectively and Q_p and Q_s are respectively the partition functions of a single molecule of polymer and solvent. The volume ratio of a solvent molecule to a polymer molecule is characterized by α , the volume of a polymer segment is represented by ρ_0^{-1} and the polymerization degree is accounted for by N .

The Florry Huggins parameter χ expresses the separation degree, chemistry of solvent molecules and segments of polymer and is inversely proportional to temperature. $w_{s,p}(r)$ is a function of interaction between molecules of solvent and segments of polymer with other solvent molecules and other polymeric segments respectively, and also the type of mean field theory of SCF.

The derivations of equation (57) in relation to the mentioned functions create a set of nonlinear equations and are solved using an appropriate equation of state with regard to a polymeric system through the self consistent method from which the energy of a two phase system is obtained [3, 38]. Furthermore, the incorporation of this theory in various studies for the analysis of nucleation phenomenon in polymeric solutions will be reviewed.

The principal reasons for the inconsistency between the results of classical nucleation theory and experiments are neglecting the effect of cell size reduction and surface curvature on the interfacial tension and the error occurring in the calculation of volume energy difference of nucleus and bulk (pressure difference).

The SCF theory is a microscopic model which includes the degrees of molecular freedom and is a suitable alternative for the classical nucleation theory. Therefore, in most studies the results of these two theories are compared and the insufficiency of the classical nucleation theory for a close prediction of results due to underlying microscopic reasons is discussed. Furthermore, the results of this theory are not usually comparable to the

experimental data and can merely be used for a qualitative analysis and evaluation of the trends of the effective parameters. Actually, SCFT provides an upper bound on the cell density, with experiment expected to find lower values of cell density. If one is interested in nanocellular foams for example, one can use SCFT to avoid spending too much time experimentally searching points of the parameter space for which SCFT maximal cell density predictions are low and concentrate on areas where the cell density has the possibility of being high[3, 38].

In one research, the interfacial tension and the volumetric energy difference are calculated using SCFT and subsequently the obtained figures are put into the energy relation of the classical nucleation theory. The application of the classical nucleation theory means accepting of the initial assumptions, i.e. a distinctive dividing surface between the nucleus and the bulk. The nucleation energy can also be calculated directly from solving equation (58) which represents the free energy of a solvent nucleus in a polymeric matrix. According to the figure (7), the classical nucleation theory overestimates the critical radius and the nucleation energy.

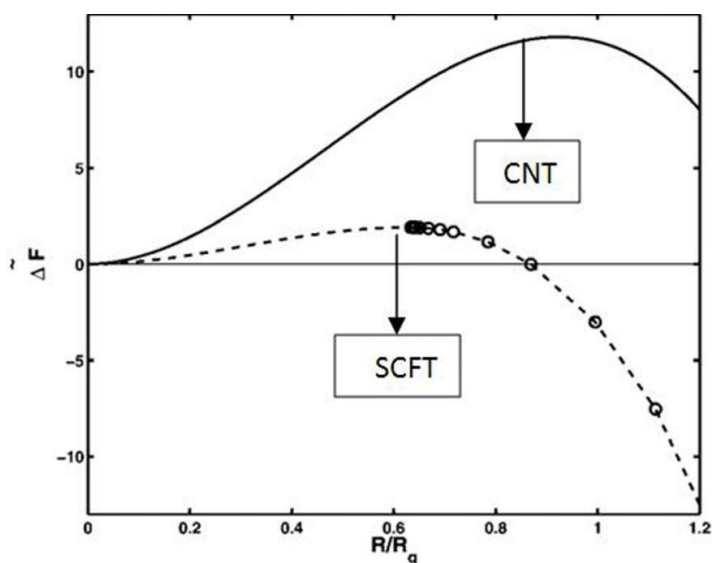


FIG7. COMPARING OF CHANGE OF NUCLEATION ENERGY WITH NUCLEUS RADIUS IN CNT AND SCFT

Actually the application of the SCF theory presents a possibility for introducing the effect of curvature of interface in scale of polymer molecules on the interfacial tension and nucleation energy. Increase of polymer molecules conformation (enhanced entropy) and reduction of internal energy reduce interfacial tension and nucleation energy [38].

In another research, the SCF theory has been used for the estimation of critical nucleation energy, critical size and density of cells. The principal purpose of this study was the achievement of an experimental method for the manufacture of a foam structure with high quality with unique characteristics such as smallest possible cell size, maximum interfacial area and nucleus with no polymeric chains. The effects of changes in the amount of the experimental parameters on the foam structure have been studied in this work. Owing to the fact that the SCF theory is based on the equilibrium statistical mechanics and does not generate any information on the kinetics of nucleation, it is therefore not a suitable method for the prediction of theoretical results and their comparison to experimental data. It can merely assess the conditions for the development of foam with an ideal structure from theoretical and qualitative point of views. In addition, the resultant information from the SCF theory are applicable for molecular analysis, deep understanding of nucleation phenomenon, identification of experimental methods and experimental conditions and reducing the number of experiments[3].

Conclusion

Based on literature the physical foaming of thermoplastics consists of first forming a saturated mixture of solvent and the polymer and then by changing the free energy of the mixture by a pressure drop or temperature rise, producing a two phase mixture consisting of solvent molecules in gas state surrounded by a polymeric layer. In this process the change in free energy of the states, after and before the spherical gas nucleus formation in polymer bulk is calculated using nucleation theories.

The main theory that has been used for this process is the classical nucleation theory. The controlling terms in using this theory for thermoplastic foaming process are interfacial tension and pressure difference between gas nucleus and polymer layer. Inaccurate and/or incorrect calculation of these terms, like neglecting the effect of polymer chains on the free energy of the system or disregarding the effects of time and pressure drop rate, are the main reasons for the inconsistency between the results of this theory and the experimental data. CNT is commonly used for prediction of thermoplastic foaming nucleation rate and its energy terms are mainly calculated using a suitable equation of state.

In the density function theory, the assumption of the existence of a dividing surface between the nucleus and the initial phase and the related errors are eliminated. In this theory, nucleation is considered as a local fluctuation density and there is no boundary between new and old phases. In addition, the free energy of the system is calculated based on the fluctuations of density of the components. This theory is used in many cases for the evaluation of nucleation phenomenon in phase transitions. In some investigations the effects of size and surface curvature of nucleus and experimental conditions on interfacial tension have been assessed using this theory and the obtained results have been incorporated in the classical nucleation theory. Additionally, the nucleation energy calculated directly using this theory appears to be lower than its equivalent calculated using the classical nucleation theory which can decrease the inconsistency between the results of this theory and the experimental data. It should be stated that, this theory has not yet been evaluated with reference to experimental results and it is merely used for the study of nucleation in molecular scales. This theory is been used recently in a preliminary work for prediction of nucleation in thermoplastic foam.

The variations of free energy of a polymeric solution with changes of components composition is expressed through the mean field theory of SCF. This theory has shown the potential to incorporate the effects of interfacial surface curvature in the scale of polymer molecules and it has been used to assess the critical energy of nucleation, critical size and density of cells. The SCFT is not considered as an appropriate method for the prediction of theoretical results and its comparison to experimental data could merely be used for the evaluation of the conditions for obtaining foams with ideal structures from the theoretical and qualitative point of views.

In computations using DFT and SCFT methods for homopolymer foams, the size of the formed nuclei in the nucleation stage is estimated to be less than 10 nm[3,38,104-105], while the results from the electron microscopic images of homopolymer foams indicate cell sizes of about 1 μm or more. If we accept the computational results of mentioned theories and assume that the nuclei formed in the nucleation stage in homopolymer foams are less than 10 nm, the produced foams must have certainly passed the growth stage as well as the nucleation stage. Therefore, the available equipments do not have the capability to record the nucleation stage in homopolymer foams. Also the nucleation rate deduced from the classic nucleation theory are completely incorrect, because its content is even less than the reported experimental rate from the SEM images.

It can be presumed that nucleation has taken place completely in homopolymer foams and the next set of events after the nucleation stage and during the growth stage determine the structure of the foam. In fact, solvent molecules are dispersed between polymer chains and have a much higher mobility. With the beginning of pressure reduction, in solvent molecules phase transition will take place from the super critical state with higher density to a gas state with lower density through nucleation mechanism and the initial nuclei will be formed with sizes less than 10 nm.

Since first order phase transition of solvent with nucleation mechanism is the controlling factor for the nucleation stage, the surface tension between the gas and super critical state of the solvent molecules is negligible, resulting in a very small nucleation energy, thus, the nucleation efficiency and density can be considered very close or even the same in foams with equal solvent absorption. After nucleation, the shaped nuclei tend to grow and escape from the bulk to decrease chemical potential difference.

The nuclei are placed in the free volume between polymer chains and in order to escape and grow they need to overcome the chain movement energy (chain elastic energy) and they make their way out through the movement of entanglements and chain slippage. Therefore there is a conflict between nuclei growth energy and elastic energy of chains where the domination of each of these energies determines the size and structure of the cells. Foam structure will be stabilized in case of temperature reduction in foam to less than the glass transition temperature of gas and polymer mixture.

Thus it seems that a model with the ability to predict the conflict between the two mentioned energies for the prediction of final cell density will be best suited.

REFERENCES

- [1] Klempner D., Frisch Kc., *Handbook of Polymeric Foams and Foam Technology* (New York: Oxford University Press, 1991)
- [2] Colton Js., Suh Np., "The Nucleation of Microcellular Thermoplastic Foam With Additives. Part I. Theoretical Considerations". *Polymer Engineering Science* 27, (1987): 485, <http://onlinelibrary.wiley.com>.
- [3] Kim Y., Park Cb., Chen P., Thompson Rb. "Towards Maximal Cell Density Predictions For Polymeric Foams." *Polymer* 52, (2011): 5622, <http://elsevier.com>.
- [4] Janani H., Famili MHn. "Investigation of a Strategy for Well Controlled Inducement of Microcellular and Nanocellular Morphologies in Polymers." *Polymer Engineering Science* 10, (2010): 1558, <http://onlinelibrary.wiley.com>.
- [5] Maghsoud Z., Famili MHn., "Phase Diagram Calculations of Water/Tetrahydrofuran/Poly(vinyl chloride) Ternary System Based on a Compressible Regular Solution Model." *Iranian Polymer Journal* 19, (2010): 581, <http://springer.com>.
- [6] Enayati Ms., Famili MHn., Janani H., "Production of Polystyrene Open-Celled Microcellular Foam in Batch Process by Supercritical CO₂." *Iranian Journal of Polymer Science and technology (Persian)* 23, (2010): 223-234.
- [7] Famili MHn., Ako M., "the Effect of Shear Rate on Dissolution of Gas and Cell Density in Continuous Foaming Process." *Iranian Journal of Polymer Science and technology (Persian)* 22, (2009): 209-215.
- [8] Enayati Ms., Famili MHn., Janani H., "Open-Celled Microcellular Foaming and the Formation of Cellular Structure by a Theoretical Pattern in Polystyrene." *Iranian Polymer Journal* 22, (2013): 417. <http://springer.com>.
- [9] Gutierrez C., Rodriguez Jf., Gracia I., "Development of a Strategy for the Foaming of Polystyrene Dissolutions in scCO₂." *Journal of Supercritical Fluids* 76, (2013): 126, <http://elsevier.com>.
- [10] Morisaki M., Ito T., Hayvali M., Tabata I., "Preparation of Skinless Polymer Foam with Supercritical Carbon Dioxide and its Application to a Photoinduced Hydrogen Evolution System." *Polymer* 49, (2008): 1611, <http://elsevier.com>.
- [11] Jacobs Ma., Kemmere Mf., "Foam Processing of Poly (ethylene-co-vinyl acetate) Rubber Using Supercritical Carbon Dioxide." *Polymer* 45, (2004): 7539, <http://elsevier.com>.
- [12] Siripurapu S., Gay Yj., Royer Jr., "Generation of Microcellular Foams of PVDF and its Blends Using Supercritical Carbon Dioxide in a Continuous Process." *Polymer* 43, (2002): 5511, <http://elsevier.com>.
- [13] Zhai W., Yu J., He J., "Ultrasonic Irradiation Enhanced Cell Nucleation: An Effective Approach to Microcellular Foams of Both High Cell Density and Expansion Ratio." *Polymer* 49, (2008): 2430, <http://elsevier.com>.
- [14] Liu T., Li D., Zhao L., "Manipulation of Polymer Foam Structure Based on CO₂-Induced Changes in Polymer Fundamental Properties." *Particuology* 8, (2010): 607, <http://elsevier.com>.
- [15] Bao Mb., Liu T., Zhao L., "A Two-Step Depressurization Batch Process for the Formation of Bi-Modal Cell Structure Polystyrene Foams Using scCO₂." *Journal of Supercritical Fluids* 55, (2011): 1104, <http://elsevier.com>.
- [16] Sato Y., Takikawa T., Takishima S., Masuoka H., "Solubilities and Diffusion Coefficients of Carbon Dioxide in Poly(vinyl acetate) and Polystyrene." *Journal of Supercritical Fluids* 19, (2001): 187, <http://elsevier.com>.
- [17] Oxtoby Dw., "Nucleation of First-Order Phase Transitions." *Accounts of Chemical Research* 31, (1998): 91, <http://pubs.acs.org>.
- [18] Fang J., Kiran E., "Kinetics of Pressure-Induced Phase Separation in Polystyrene + Acetone Solutions at High Pressures." *Polymer* 47, (2006): 7943, <http://elsevier.com>.
- [19] Zakian Se., Famili MHn., "Controlling foam morphology of polystyrene via surface chemistry, size and concentration of nanosilica particles." *Journal of Materials Science* 49, (2014): 6225, <http://springer.com>.
- [20] Mokhtari M., Famili MHn., "The effect of pressurized and fast stabilization on one step batch foaming process for the investigation of cell structure formation." *The Journal of Supercritical Fluids* , (2003): DOI: 10.1016/j.supflu.2015.11.023. <http://elsevier.com>.
- [21] Barikani M., Mirza TM., Tavakoli A., "Synthesis and Characterization of Suitable Resole for Preparation of Phenolic Foam." *Iranian Journal of Polymer Science and technology (Persian)* 16, (2004): 319-325.

- [22] Shafieizadegan EAr., Katbab Aa., Dehkhoda P., Karami Hr., Barikani M., Sadeghi SHh., Ghorbani A., "Preparation and Characterization of Foamed Polyurethane/Silicone Rubber/Graphite Nanocomposite as Radio Frequency Wave Absorbing Material: The Role of Interfacial Compatibilization." *Composite Science Technology* 72, (2012): 382, <http://elsevier.com>.
- [23] Park Cb., Behraves Ah., Venter Rd., "Low Density Microcellular Foam Processing in Extrusion Using CO₂." *Polym Engineering Science* 38, (1998): 1812, <http://onlinelibrary.wiley.com>.
- [24] Park Cb., Behraves Ah., Venter Rd., Cheung Lk., "Extrusion of Polypropylene Foams with Hydrocerol and Isopentane." *Journal of Vinyl and Additive Technology* 2, (1996): 349, <http://onlinelibrary.wiley.com>.
- [25] Mahmoodi M., Behraves Ah., Rezavand Sam., Golzar M., "Theoretical and Visual Study of Bubble Dynamics in Foam Injection Molding." *Polymer Engineering and Science* 50, (2010): 561, <http://onlinelibrary.wiley.com>.
- [26] Colton Js., Suh Np., "Nucleation of Microcellular Foam: Theory and Practice." *Polymer Engineering and Science* 27, (1987): 500, <http://onlinelibrary.wiley.com>.
- [27] Colton Js., Suh Np., "the Nucleation of Microcellular Thermoplastic Foam with Additives. Part II. Experimental Results and Discussion." *Polymer Engineering and Science* 27, (1987): 493, <http://onlinelibrary.wiley.com>.
- [28] Tomasko Dl., Burley A., "Development of CO₂ for Polymer Foam Applications." *Journal of Supercritical Fluids* 47, (2009): 493, <http://elsevier.com>.
- [29] Kashchiev D., *Nucleation: Basic Theory with Applications* (UK: Butterworth-Heinemann, 2000)
- [30] Vehkamäki H., *Classical Nucleation Theory in Multicomponent Systems* (Finland: Springer, 2006)
- [31] Riahinezhad M., Ghasemi I., Karrabi M., Azizi H., "An Investigation on the Correlation Between Rheology and Morphology of Nanocomposite Foams Based on Low-Density Polyethylene and Ethylene Vinyl Acetate Blends." *Polymer Composite* 31, (2010): 1808, <http://onlinelibrary.wiley.com>.
- [32] Ghasemi I., Farsheh At., Masoomi Z., "Effects of Multi-Walled Carbon Nanotube Functionalization on the Morphological and Mechanical Properties of Nanocomposite Foams Based on Poly(vinyl chloride)/(wood flour)/ (multi-walled carbon nanotubes)." *Journal of Vinyl and Additive Technology* 18, (2012): 161, <http://onlinelibrary.wiley.com>.
- [33] Minaei-Zaim M., Ghasemi I., Karrabi M., Azizi H., "Effect of Injection Molding Parameters on Properties of Cross-Linked Low-Density Polyethylene/Ethylene Vinyl Acetate/Organoclay Nanocomposite Foams." *Iranian Polymer Journal* 21, (2012): 537, <http://springer.com>.
- [34] Keramati M., Ghasemi I., Karrabi M., Azizi H. "Microcellular Foaming of PP/EPDM/Organoclay Nanocomposites: the Effect of the Distribution of Nanoclay on Foam Morphology." *Iranian Polymer Journal* 44, (2012): 433, <http://springer.com>.
- [35] Keramati M., Ghasemi I., Karrabi M., Azizi H., Production of microcellular foam based on PP/EPDM: The effects of processing parameters and nanoclay using response surface methodology. *European Polymer Journal* 12, (2012): 612, <http://elsevier.com>.
- [36] Humphrey Jm., "Introduction to the Physics of Nucleation." *Comptes Rendus Physique* 7, (2006): 946, <http://elsevier.com>.
- [37] Thompson Rb., MacDonald Jr., Chen P., "Origin of Change in Molecular-Weight Dependence for Polymer Surface Tension." *Physical Review E* 78, (2008): 030801, <http://pre.aps.org>.
- [38] Merikanto J., Lauri A., Vehkama H., "Origin of the Failure of Classical Nucleation Theory: Incorrect Description of the Smallest Clusters." *Physical Review Letter* 98, (2007): 145702, <http://prl.aps.org>.
- [39] Goel Sk., Beckman Ej., "Generation of Microcellular Polymeric Foams Using Supercritical Carbon Dioxide. I: Effect of Pressure and Temperature on nucleation." *Polymer Engineering and Science* 34, (1994): 1137, <http://onlinelibrary.wiley.com>.
- [40] Han Jh., Han Cd., "Bubble Nucleation in Polymeric Liquids. II. Theoretical Considerations." *Journal Polymer Science Part B Polymer Physics* 28, (1990): 743, <http://onlinelibrary.wiley.com>.
- [41] Kim Y, Park Cb., Chen P., Thompson Rb., "Maximal Cell Density Predictions for Compressible Polymer Foams." *Polymer* 54, (2013): 841, <http://elsevier.com>.
- [42] Cahn Jw., Hilliard Je., "Free Energy of a Nonuniform System. I. Interfacial Free Energy." *Journal of Physical Chemistry* 28, (1958): 258, <http://pubs.acs.org>.

- [43] Cahn Jw., "Free Energy of a Nonuniform System. II. Thermodynamic Basis." *Journal of Physical Chemistry* 30, (1959): 1121, <http://pubs.acs.org>.
- [44] Cahn Jw., Hilliard Je., "Free Energy of a Nonuniform System. III. Nucleation in a Two-Component Incompressible Fluid." *Journal of Physical Chemistry* 31, (1959): 688, <http://pubs.acs.org>.
- [45] Talreja M., Towards Understanding Interfacial Phenomena in Polymer-CO₂ Systems. PHD thesis, USA, The Ohio State University (2010).
- [46] Talreja M., Kusaka I., Tomasko DL., "Density Functional Approach for Modeling CO₂ Pressurized Polymer Thin Films in Equilibrium." *Journal of Physical Chemistry* 130, (2004): 084902, <http://pubs.acs.org>.
- [47] Ghosh S., Ghosh Sk., "Density Functional Theory of Size-Dependent Surface Tension of Lennard-Jones Fluid Droplets Using a Double Well Type Helmholtz FreeEnergy Functional." *Journal of Physical Chemistry* 135, (2011): 124710, <http://pubs.acs.org>.
- [48] Ghosh S., Ghosh Sk., "Homogeneous nucleation in vapor-liquid phase transition of Lennard-Jones fluids: A density functional theory approach." *Journal of Physical Chemistry* 134, (2011): 024502, <http://pubs.acs.org>.
- [49] Parra Ie., Graa Jc., "Influence of the Attractive Pair-Potential in Density Functional Models of Nucleation." *Journal of Physical Chemistry* 132, (2010): 034702, <http://pubs.acs.org>.
- [50] Kim Y., Park Cb., Chen P., Thompson Rb., "Origins of The Failure of Classical Nucleation Theory for Nanocellular Polymer Foams." *Soft Matter* 7, (2011): 7351, <http://rsc.org>.
- [51] Binder K., Müller M., Virnau P., Macdowell Lg., "Polymer + Solvent Systems: Phase Diagrams, Interface Free Energies, and Nucleation." *Advance in Polymer Science* 173, (2005): 1, <http://Springr.com>
- [52] Park H., Thompson Rb., Lanson N., Tzoganakis C., Park Cb., Chen P., "Effect of Temperature and Pressure on Surface Tension of Polystyrene in Supercritical Carbon Dioxide." *Journal of Physical Chemistry B* 111, (2007): 3859, <http://pubs.acs.org>.
- [53] Muller M., MacDowell Lg., Virnau P., Binder K., "Interface Properties and Bubble Nucleation in Compressible Mixtures Containing Polymers." *Journal of Physical Chemistry* 117, (2002): 5480, <http://pubs.acs.org>.
- [54] Kiran E., Foaming Strategies for Bioabsorbable Polymers in Supercritical Fluid Mixtures. Part II. Foaming of Poly (ϵ -caprolactone-co-lactide) in Carbon Dioxide and Carbon Dioxide + Acetone Fluid Mixtures and Formation of Tubular Foams Via Solution Extrusion." *Journal of Supercritical Fluids* 54, (2010): 308, <http://elsevier.com>.
- [55] Han Jh., Han Cd., "Bubble Nucleation in Polymeric Liquids. I. Bubble Nucleation in Concentrated Polymer Solutions." *Journal of Polymer Science Part B Polymer Physics* 28, (1990): 711, <http://onlinelibrary.wiley.com>.
- [56] Zhang W., Phase Behavior and Phase Separation Kinetics in Polymer Solutions under High Pressure. PHD thesis, Virginia Polytechnic Institute and State University, USA, (2005).
- [57] Lefebvre Aa., Lee Jh., Jeon Hs., Balsara Np., "Initial Stages of Nucleation in Phase Separating Polymer Blends." *Journal of Physical Chemistry* 111, (1999): 6082, <http://pubs.acs.org>
- [58] Hatanaka M., Saito H., "In-Situ Investigation of Liquid-Liquid Phase Separation in Polycarbonate/Carbon Dioxide System." *Macromolecules* 37, (2004): 7358, <http://pubs.acs.org>
- [59] Lora M., McHugh Ma., "Phase Behavior and Modeling of the Poly Methyl Methacrylate -CO₂-Methyl Methacrylate System." *Fluid Phase Equilibria* 157, (1999): 285, <http://elsevies.com>
- [60] Ozkan Ia., Teja As., "Phase Equilibria in Systems with Specific CO₂+ Polymer Interaction." *Fluid Phase Equilibria* 228, (2005): 487, <http://elsevies.com>.
- [61] Kasturirangan A., Grant C., Teja AS., "Compressible Lattice Model for Phase Equilibria in CO₂ Polymer Systems." *Industrial & Engineering Chemistry Research* 47, (2008): 645, <http://pubs.acs.org>.
- [62] Kasturirangan A., Teja As., "Correlation of Cloud Points in CO₂ Fluorinated Polymer Systems." *Journal of Chemical & Engineering Data* 55, (2010): 4385, <http://pubs.acs.org>.

- [63] Kasturirangan A., Koh Ca., Teja As., "Glass-Transition Temperatures in CO₂ Polymer Systems: Modeling and Experiment." *Industrial & Engineering Chemistry Research* 50, (2011): 158, <http://pubs.acs.org>.
- [64] Yuan Y., Teja As., "Extension of a Compressible Lattice Model to CO₂ + Cosolvent + Polymer Systems." *Journal of Supercritical Fluids* 55, (2010): 358, <http://elsevier.com>.
- [65] Tan Sp., Adidharma H., Radosz M., "Recent Advances and Applications of Statistical Associating Fluid Theory." *Industrial & Engineering Chemistry Research* 47, (2008): 8063, <http://pubs.acs.org>.
- [66] Ott Ba., Caneba G., "Solubility of Supercritical CO₂ in Polystyrene during Foam Formation via Statistical Associated Fluid Theory (SAFT) Equation of State." *Journal of Minerals & Materials Characterization & Engineering* 9, (2010): 411, www.scrip.org
- [67] Xiong Y., Kiran E., "Kinetics of Pressure-induced Phase Separation (PIPS) in Polystyrene + methylcyclohexane Solutions at High Pressure." *Polymer* 41, (2000): 3759, <http://elsevier.com>.
- [68] Zhuang W., Kiran E., "Kinetics of Pressure-Induced Phase Separation (PIPS) From Polymer Solutions by Time-Resolved Light Scattering. Polyethylene + n-Pentane." *Polymer* 39, (1998): 2903, <http://elsevier.com>.
- [69] Liu K., Kiran E., "Kinetics of Pressure-Induced Phase Separation (PIPS) in Solutions of Polydimethylsiloxane in Supercritical Carbon Dioxide: Crossover From Nucleation and Growth to Spinodal Decomposition Mechanism." *Journal of Supercritical Fluids* 16, (1999): 59, <http://elsevier.com>.
- [70] Colton Js., the nucleation of microcellular thermoplastic foam, PHD thesis, Massachusetts Institute of Technology, USA, (1985).
- [71] Mortezaie M., Famili MHn., Kokabi M., "Effect of Surface Modification of Nanosilica on the Viscoelastic Properties of its Polystyrene Nanocomposite." *Iranian Journal of Polymer Science and technology (Persian)* 6, (2009): 523-531.
- [72] Mortezaie M., Famili MHN., Kokabi M., "Influence of the Particle Size on the Viscoelastic Glass Transition of Silica-Filled Polystyrene." *Journal Applied Polymer Science* 115, (2010): 969, <http://onlinelibrary.wiley.com>.
- [73] Zakian Se., Famili MHn., Ako M., "Hetrogeneous Nucleation in Batch Foaming of Polystyrene in Presence of Nanosilica as a Nucleating Agent." *Iranian Journal of Polymer Science and technology (Persian)* 25, (2012): 232-241.
- [74] Famili MHn., Janani H., Enayati Ms., "Foaming of a Polymer-Nanoparticle System: Effect of the Particle Properties." *Journal Applied Polymer Science* 119, (2011): 2847, <http://onlinelibrary.wiley.com>.
- [75] Mortezaie M., Famili MHn., Kalae Mr., "Effect of Immobilized Interfacial Layer on the Maximum Filler Loading of Polystyrene/Silica Nanocomposites." *Journal of Reinforced Plastic and Composite* 30, (2011): 593, <http://jrp.sagepub.com>.
- [76] Hwang Ss., Peming Ph., "Effects of Silica Particle Size on the Structure and Properties of Polypropylene/Silica Composites Foams." *Industrial of Engineering Chemistry Research* 19, (2013): 1377, <http://pubs.acs.org>.
- [77] Zeng C.h., Hossieny N., Wang B., "Morphology and Tnsile Properties of PMMA Carbon Nanotubes Nanocomposites and Nanocomposites Foams." *Composite Science and Technology* 82, (2013): 29, <http://elsevier.com>.
- [78] Costeux S., Zhu L., "Low Density Thermoplastic Nanofoams Nucleated by Nanoparticles." *Polymer* 54, (2013): 2785, <http://elsevier.com>.
- [79] Soares Fa., Nachtigall Sm., "Effect of Chemical and Physical Foaming Additives on the Properties of PP/wood Flour Composites." *Polymer Testing* 32, (2013): 640, <http://elsevier.com>.
- [80] Nofar Mr., Tabatabaei Ar., Park Cb., "Effects of Nano-/Micro-Sized Additives on the Crystallization Behaviors of PLA and PLA/CO₂ mixtures." *Polymer* 54, (2013): 2382, <http://elsevier.com>.
- [81] Goren K., Chen L., Ozisik R., "Influence of Nanoparticle Surface Chemistry and Size on Supercritical Carbon Dioxide Rocessed Nanocomposite Foam Morphology." *Journal of Supercritical Fluids* 51, (2010): 420, <http://elsevier.com>.
- [82] Salerno A., Maio E., Iannace S., Netti Pa., "Solid-State Supercritical CO₂ Foaming of PCL and PCL-HA Nano-composite: Effect of Composition, Thermal History and Foaming Process on Foam Pore Structure." *Journal of Supercritical Fluids* 58, (2011): 158, <http://elsevier.com>.

- [83] Thanh V., Duchet J., Gerard J., "Processing of Nanocomposite Foams in Supercritical Carbon Dioxide. Part I: Effect of Surfactant." *Polymer* 51, (2010): 3436, <http://elsevier.com>.
- [84] Zeng Ch., Hossieny N., Wang B., "Synthesis and Processing of PMMA Carbon Nanotube Nanocomposite Foams." *Polymer* 51, (2010):655, <http://elsevier.com>.
- [85] Chen L., Ozisik R., Schadler Ls., "The Influence of Carbon Nanotube Aspect Ratio on the Foam Morphology of MWNT/PMMA Nanocomposite Foams." *Polymer* 51, (2010): 2368, <http://elsevier.com>.
- [86] Kim Sg., Siu Nl., Chul Bp., Sain M., "The Effect of Dispersed Elastomer Particle Size on Heterogeneous Nucleation of TPO with N₂ Foaming." *Chemical Engineering Science* 66, (2011): 3675, <http://elsevier.com>.
- [87] Shukla Sh., Koelling Kw., "Classical Nucleation Theory Applied to Homogeneous Bubble Nucleation in the Continuous Microcellular Foaming of the Polystyrene-CO₂ System Polymer nanocomposite foams." *Industrial of Engineering Chemistry Research* 48, (2009): 7603, <http://pubs.acs.org>.
- [88] Gang Zc., "Irreversible Thermodynamics of Nucleation." *Journal of Colloid and Interface Science* 124, (1988): 262, <http://elsevier.com>.
- [89] Kweeder Ja., Nucleation Mechanism in Microcellular Polymer foam. PHD thesis, Clarkson University, USA, (1997).
- [90] Schmelzer JWP., Baidakov Vg., "Classical and Generalized Gibbs' Approaches and the Work of Critical Cluster Formation in Nucleation Theory." *Journal of Physical Chemistry* 124, (2006): 194503, <http://pubs.acs.org>.
- [91] Schmelzer JWP., Baidakov Vg., "on Different Possibilities of a Thermodynamically Consistent Determination of the Work of Critical Cluster Formation in Nucleation Theory." *Journal of Physical Chemistry* 119, (2003): 10759, <http://pubs.acs.org>.
- [92] Schmelzer JWP., Abyzov As., "Generalized Gibbs' Approach to the Thermodynamics of Heterogeneous Systems and the Kinetics of First-Order Phase Transitions." *Journal of Engineering Thermophysics* 16, (2003): 119, <http://springer.com>.
- [93] Baidakov Vg., Boltashev GSh., Schmelzer JWP., "Comparison of Different Approaches to the Determination of the Work of Critical Cluster Formation." *Journal of Colloid and Interface Science* 231, (2000): 312, <http://elsevier.com>.
- [94] Schmelzer JWP., Gutzow Is., "Reconciling Gibbs and Van der Waals: A New Approach to Nucleation Theory." *Journal of Physical Chemistry* 112, (2000): 3820, <http://pubs.acs.org>.
- [95] Liao X., Yaogai Gl., Park Cb., Chen P., "Interfacial tension of linear and branched PP in supercritical carbon dioxide." *Journal of Supercritical Fluids* 55, (2010): 386, <http://elsevier.com>.
- [96] Wasai K., Kaptay G., Mukaic K., Shinozaki N., "Modified Classical Homogeneous Nucleation Theory and a New Minimum in Free Energy Change 2. Behavior of Free Energy Change with a Minimum Calculated for Various Systems." *Fluid Phase Equilibria* 255, (2007): 55, <http://elsevier.com>.
- [97] Schmelzer JWP., "Comments on the Nucleation Theorem." *Journal of Colloid and Interface Science* 242, (2001): 354, <http://elsevier.com>.
- [98] Panayiotou C., Pantoula M., Stefanis E., Tsivintzelis I., "Nonrandom Hydrogen-Bonding Model of Fluids and Their Mixtures. 1. Pure Fluids." *Industrial of Engineering Chemistry Research* 43, (2004): 6592, <http://pubs.acs.org>.
- [99] Panayiotou C., Tsivintzelis I., Economou Ig., "Nonrandom Hydrogen-Bonding Model of Fluids and Their Mixtures. 2. Multicomponent Mixtures." *Industrial of Engineering Chemistry Research* 46, (2007): 2628, <http://pubs.acs.org>.
- [100] Siripurapu S., Coughlan Ja., Spontak Rj., "Surface-Constrained Foaming of Polymer Thin Films with Supercritical Carbon Dioxide." *Macromolecules* 37, (2004): 9872, <http://pubs.acs.org>.
- [101] Sadowski G., Arlt W., "High-Pressure Phase Equilibrium in Multi-Component Hydrocarbon Systems Using the MFLG Model." *Journal of Supercritical Fluids* 8, (1995): 273, <http://elsevier.com>.
- [102] Oxtoby Dw., "Density Functional Methods in the Statistical Mechanics of Materials." *Annual Review of Materials Research* 32, (2002): 39-52.
- [103] Oxtoby Dw., "Nonclassical Nucleation Theory for the Gas-Liquid Transition." *Journal of Physical Chemistry* 89, (1988): 7521, <http://pubs.acs.org>.

- [104] Xiaofei Xu., Diego Ec., Stéphane C., "Discontinuous Bubble Nucleation Due to a Metastable Condensation Transition in Polymer-CO₂ Mixtures." *The Journal of Physical Chemistry Letters* 4, (2013): 1639, <http://pubs.acs.org>.
- [105] Xiaofei Xu., Diego Ec., "Bubble Nucleation in Polymer-CO₂ Mixtures." *Soft Matter* 9, (2013): 9675, <http://rsc.org>.
- [106] Matsen Mw., *Self-Consistent Field Theory and Its Applications*(Germany: Wiley-VCH: 2005)
- [107] Helfand E., "Theory of Inhomogeneous Polymers: Fundamentals of the Gaussian Randomwalk Model." *Journal of Physical Chemistry* 62 ,(1975): 999, <http://pubs.acs.org>.
- [108] Wood Sm., Wang Zg., "Nucleation in Binary Polymer Blends: A Self-Consistent Field Study." *Journal of Physical Chemistry* 116, (2002): 2289, <http://pubs.acs.org>.
- [109] Ozkan Ia., Thermodynamic model for associating polymer solutions. PHD thesis, Georgia Institute of Technology, USA, (2004).
- [110] Kasturirangan A., specific Interaction in carbon dioxide + polymer solutions. PHD thesis, Georgia Institute of Technology, USA, (2007).